Unit cell expansion in Laves phase-type compounds caused by interstitial hydrogen

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The Laves phase-type compounds of yttrium and rare earths with manganese (RMn$_2$) easily absorb hydrogen which locates at the interstitial sites. It is well known that the lattice expands with increasing hydrogen concentration and the volume increases up to about 30%. The increase of the unit volume is nonlinear as a function of hydrogen content. To explain this behaviour a model in which the volume changes were correlated with the changes of the bulk modulus with hydrogen concentration was proposed by Hirata and co-workers. This model describes properly the initial volume increase, but does not reflect the changes at higher concentrations. For the hydrides with R = Y, Gd, Dy, Tb, Ho at $x \approx 3$ the volume of AB$_3$ interstitials becomes large enough for hydrogen to enter. According to this observation we extended this model. We show that the calculated volume expansion fits very well to the experimental data for RMn$_2$ (R = Y, Gd, Dy, Tb, Ho).

1 Introduction

The Laves phase-type compounds of yttrium and rare earths with manganese (RMn$_2$) easily absorb hydrogen which locates at the interstitial sites. It is well known that the lattice expands with increasing hydrogen concentration and the volume increases up to about 30%. The increase of the unit cell volume found experimentally in the series of RMn$_2$H$_x$ hydrides appears to be a nonlinear function of hydrogen content. This effect was reported for Y [1, 2], Gd [3], Dy [4], Tb [5] and Ho [6]. For RFe$_2$H$_x$ similar behaviour of the unit cell expansion was observed, as reported for Y [7] and Er and Tb (e.g. [8]). The theoretical approach to the problem of volume expansion in metallic hydrides is presented, for example, in [9]. It is assumed that the hydrogen atoms which are practically incompressible cause the unit volume expansion $\Delta V_H$. Taking into account the transfer of the electrons from hydrogen atoms to the d-band, the interaction and modification of the d-band electron density results in changes of the Fermi energy $\Delta E_F$ causing volume reduction $\Delta V_e$, which according to [9] reaches roughly 30% of $\Delta V_H$. For $n(E_F)$ not influenced by the transfer of electrons from hydrogen atoms it is concluded that the volume should increase linearly with hydrogen content, and for the cases where $n(E_F)$ changes with hydrogen content a decrease of volume expansion with increasing hydrogen content becomes possible. However, no quantitative model relating $\Delta V/V$ with $x$ has been given for the nonlinear case. To explain such specific behaviour for Mn-based compounds, Hirata et al. [9] proposed recently a model in which they related the hydrogen-induced volume changes to the changes of the bulk modulus with hydrogen concentration. As far as the change of bulk modulus can be related with changes of intrinsic properties, both approaches are com-
This model describes properly the initial volume increase but does not reflect the changes at higher concentrations, which is what motivated the present work.

2 Model of Hirata

The model of Hirata is based on the concept of bulk compressibility where pressure is replaced by hydrogen concentration to obtain the expansion of the unit cell. Recently Hirata et al. [9] proposed the equation of the form

$$\frac{V}{V_0} = \left( \frac{B_0 + bx}{B_0} \right)^{1/b},$$

for describing relative unit cell volume change with hydrogen concentration $x$ for Laves-phase hydrides $\text{RMn}_2\text{H}_x$. $B_0$ is a parameter of the lattice contraction, a quantity analogous to the bulk modulus at starting concentration related to the intrinsic pressure, and $b$ is the first derivative with respect to concentration ($B_x = B_0 + bx$). The model was used to describe volume changes for Y, Gd, Tb and Dy.

3 Our model

The structure is a body-centred cubic one and belongs to the Fd3m (O7h) space group. The cell contains 16 Mn atoms at 16d positions (local symmetry 3m; smaller spheres in Fig. 1) and 8 Y atoms at 8a positions (local symmetry 43m; larger spheres in Fig. 1). The Mn nearest neighbours are 6 Mn atoms, 6 Y atoms and 4 Mn atoms. The hydrogen atoms can enter $\text{A2B2}$, $\text{AB3}$ or $\text{B4}$ interstitial positions depending on their volumes. It is well known that in these hydrides hydrogen atoms enter at the first the $\text{A2B2}$ type interstitial sites. In many works and discussions the possibility of hydrogen entering into $\text{AB3}$ interstitial positions is assumed and considered for $x \approx 3$ even if $\text{A2B2}$ sublattice is not filled. With account being taken of the Switendick criterion, one should expect up to $x = 6$ hydrogen atoms/ formula unit. However, due to expansion caused by hydrogen at $\text{A2B2}$ interstitial sites, the volumes of $\text{AB3}$ interstitials may become large enough according to the Westlake criterion and start to accept hydrogen atoms. According to this idea we assume that entry of hydrogen into $\text{AB3}$ interstitial sites begins at a specific concentration $X_c$ and causes the same type of tension as in the case of hydrogen atoms entering into $\text{A2B2}$ sites. Thus we propose the relation

$$\frac{\Delta V}{V_0} = \left( \frac{B_0 + bx}{B_0} \right)^{1/b} - 1 \quad \text{for} \quad x < X_c,$$

$$\frac{\Delta V}{V_0} = \left( \frac{B_0 + b(X_c + (1-P)(x-X_c))}{B_0} \right)^{1/b} + \left( \frac{B_0 + Pb(x-X_c)}{B_0} \right)^{1/b} - 2 \quad \text{for} \quad x \geq X_c,$$
where $X_c$ is the concentration for which the AB3 interstitial sites become large enough for hydrogen to enter and $P$ is the probability of filling the AB3 sites by hydrogen atoms for concentrations greater than $X_c$ ($P = 0$ for $x \leq X_c$).

The parameters of our model and that of Hirata are compared in Table 1, and the fits are presented in Fig. 2 for YMn$_2$H$_x$, DyMn$_2$H$_x$, GdMn$_2$H$_x$, TbMn$_2$H$_x$, and HoMn$_2$H$_x$. For the compounds with Sm, Nd, and Er, there are not enough experimental data to fit the improved model. For the experimental data for hydrogen concen-
Table 1 Fitted parameters for the discussed models.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hirata model</th>
<th>Our model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B_0$</td>
<td>$b$</td>
</tr>
<tr>
<td>YMn$_2$H$_x$</td>
<td>11.69</td>
<td>5.09</td>
</tr>
<tr>
<td>DyMn$_2$H$_x$</td>
<td>9.12</td>
<td>5.25</td>
</tr>
<tr>
<td>GdMn$_2$H$_x$</td>
<td>13.50</td>
<td>3.78</td>
</tr>
<tr>
<td>TbMn$_2$H$_x$</td>
<td>11.05</td>
<td>4.11</td>
</tr>
<tr>
<td>HoMn$_2$H$_x$</td>
<td>10.41$^a$</td>
<td>3.88$^a$</td>
</tr>
</tbody>
</table>

$^a$ Fitted by the authors using Hirata’s formula.

For $x > 3$ the increase of the volume is greater than expected from the simple Hirata model, worsening the fit. For the improved model, as one can see from Fig. 2, in spite of the fact that there are relatively few experimental points, the improvement of the fits is clearly visible. The values of the characteristic $X_c$ are indeed close to 3 (3.06–3.33) for all compounds, and the probabilities of entering the AB3 interstitial sites are also reasonable. From the microscopic point of view it can be understood that the volume of hydrogen at AB3 is different from that for A2B2 and that the electrons in this case modify the electronic structure accordingly.

It is also interesting that in the family of Laves-phase hydrides YFe$_2$H$_x$ a very similar, but not so distinct, $\Delta V/V$ dependence on hydrogen content is apparent [7].

The possibility of the magnetovolume effect should be considered for $x > 3$, because for most of these compounds the magnetic ordering temperature increases with hydrogen concentration and passes 300 K for $x \sim 3$. However, for GdMn$_2$H$_x$, $T_c$ is $\sim 300$ K for $x \sim 2$, so the magnetovolume effect should be observed already at lower concentration. On the other hand there is a well-known critical Mn–Mn distance for localisation of Mn magnetic moments ($d = 2.66$ Å), which means that already for all RMn$_2$H$_x$ hydrides with $x > 1$ the Mn moments are localised and the magnetic ordering temperature increases linearly with Mn–Mn distance [7]. The opposite tendency of decreasing magnetic ordering temperature is observed for RFe$_2$H$_x$, whereas $\Delta V/V$ changes with hydrogen concentration for YFe$_2$H$_x$ are similar to those observed for RMn$_2$H$_x$. With account being taken of these observations, we assumed that the magnetovolume effect is not responsible for the observed volume changes.

**Fig. 3** Fit parameters as a function of atomic radius: a) $B_0$, b) $P$. The experimental points (from left to right) correspond to the elements Ho, Dy, Tb and Gd.
It was also interesting to look at the correlations between the fit parameters and the atomic radius in the rare earth series. We observe an increase of the $B_0$ parameter as a function of atomic radius of rare earth atoms (Fig. 3a) which corresponds to the increase of the strain of the lattice.

The decrease of probability $P$ with atomic radius (Fig. 3b) reflects the fact that the size of the corresponding interstitial sites increases, which means that for lower hydrogen concentration AB3 interstitials are opened for hydrogen. The $B_0$ derivative $b$ and parameter $X_c$ also seem to change, but due to too large fitting errors we cannot draw any conclusions about correlations.

4 Conclusions

The proposed improvement of the Hirata model gives better fit to the published data for RMn$_2$H$_x$ compounds. Also, for $x > 3$ the AB3 interstitial size calculated for the appropriate lattice parameters is greater than 0.4 Å in agreement with Westlake’s criterion, which supports the presented model.

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References